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PTO/SB/05 (4/98)

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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No.	033808.137
First Inventor or Application Identifier	C. LACROIX and A. BOUILLOUX
Title	THERMOPLASTIC POLYESTER COMPOSITIONS HAVING IMPROVED IMPACT PROPERTIES
Express Mail Label No.	N/A

APPLICATION ELEMENTS

See MPEP chapter 1500 concerning design patent application contents.

ADDRESS TO Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

1. ☒ *Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original, and a duplicate for fee processing)

2. ☒ Specification [*Total Pages* 18]
(preferred arrangement set forth below, MPEP 1503.01)
- Descriptive title of the Invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure

3. ☒ Drawing(s) (35 U.S.C.113) - FORMAL - [*Total Sheets* 3]

4. ☐ Oath or Declaration [*Total Pages*]
a. ☐ Newly executed (original or copy)
b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))*(for continuation/divisional with Box 16 completed)*
i. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 133(b).

5. ☐ Microfiche Computer Program (Appendix)

6. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
a. ☐ Computer Readable Copy
b. ☐ Paper Copy (identical to computer copy)
c. ☐ Statement verifying identity of above copies

*** NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).**

ACCOMPANYING APPLICATIONS PARTS

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R.§3.73(b) Statement *(when there is an assignee)* ☐ Power of Attorney
9. ☐ English Translation Document *(if applicable)*
10. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☒ Copies of IDS Citations
11. ☒ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
13. ☐ *Small Entity Statement(s) *(PTO/SB/09-12)* ☐ Statement filed in prior application, Status still proper and desired
14. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
15. ☒ Other: COPY OF FRENCH PARENT APPLICATION (UNCERTIFIED)

16. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below and in a preliminary amendment:*

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: _____ /

Prior application information: Examiner _____ Group / Art Unit:

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

17. CORRESPONDENCE ADDRESS

☐ *Customer Number or Bar Code Label* *(Insert Customer No. or Attach bar code label here)* or ☐ *Correspondence address below*

Name	Frederick F. Calvetti				
	SMITH, GAMBRELL & RUSSELL, LLP				
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Name (Print/Type)	Frederick F. Calvetti	*Registration No. (Attorney/Agent)*	28,557
Signature		*Date*	11/24/2000

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FEE TRANSMITTAL for FY 2001

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TOTAL AMOUNT OF PAYMENT ($) 710

Complete if Known	
Application Number	To be Assigned
Filing Date	24 November 2000
First Named Inventor	Christophe LACROIX and Alain BOUILLOUX
Examiner Name	To be Assigned
Group / Art Unit	To be Assigned
Attorney Docket No.	033808.137

METHOD OF PAYMENT (check one)

1. ☐ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

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Deposit Account Name:

☒ Charge Any Additional Fee Required Under 37 CFR 1.16 and 1.17

☐ Applicant claims small entity status. See 37 CFR 1.27

2. ☒ Payment Enclosed:

☒ Check ☐ Credit card ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Fee Code	Large Entity Fee ($)	Small Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	710	201	355	Utility filing fee	710.00
106	320	206	160	Design filing fee	
107	490	207	245	Plant filing fee	
108	710	208	355	Reissue filing fee	
114	150	214	75	Provisional filing fee	

SUBTOTAL (1) ($) 710

2. EXTRA CLAIM FEES

			Extra Claims		Fee from below	=	Fee Paid
Total Claims	11	-20** =	0	X		=	0
Independent Claims	2	-3** =	0	X		=	0
Multiple Dependent	0			X		=	0

Large Fee Code	Large Entity Fee ($)	Small Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	80	202	40	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	80	209	40	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 0

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Fee Code	Large Entity Fee ($)	Small Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet.	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	390	216	195	Extension for reply within second month	
117	890	217	445	Extension for reply within third month	
118	1,390	218	695	Extension for reply within fourth month	
128	1,890	228	945	Extension for reply within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive – unavoidable	
141	1,240	241	620	Petition to revive – unintentional	
142	1,240	242	620	Utility issue fee (or reissue)	
143	440	243	220	Design issue fee	
144	600	244	300	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	710	246	355	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	710	249	355	For each additional invention to be examined (37 CFR § 1.129(b))	
179	710	279	355	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	
				Other fee (specify)	

*Reduced by Basic Filing Fee Paid SUBTOTAL (3) ($) 0

SUBMITTED BY				Complete *(if applicable)*	
Name (Print/Type)	Frederick F. Calvetti	*Registration No. (Attorney/Agent)*	28,557	*Telephone*	202-659-2811
Signature				*Date*	24 November 2000

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Docket 033808.137

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Christophe LACROIX and Alain BOUILLOUX

Serial No.: Unassigned

Examiner: Unassigned

Filed: Concurrently Herewith

Group Art Unit: Unassigned

For: THERMOPLASTIC POLYESTER COMPOSITIONS HAVING IMPROVED IMPACT PROPERTIES

PRELIMINARY AMENDMENT

Honorable Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to calculating the filing fee for the above-identified new U.S. patent application, kindly amend the application as follows.

IN THE SPECIFICATION:

Please amend the specification as follows.

Page 1, line 5, delete "[Field of the invention]" and insert --FIELD OF THE INVENTION--; and

line 25, delete "[Prior art]" and insert --BACKGROUND OF THE INVENTION--.

Page 3, after "EP 531,008 TABLE", delete "[The technical problem]" and insert the following:

--BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram illustrating the Charpy Impact vs AX/Core Shell ratio at -40°C;

Figure 2 is a diagram illustrating the Charpy Impact vs AX/Core Shell ratio at +23°C; and

Figure 3 is a diagram illustrating the MFI vs AX/Core Shell ratio at 250°C.--.

Page 4, line 21, delete “[Brief description of the invention]” and insert --SUMMARY OF THE INVENTION--.

Page 5, line 20, delete “[Detailed description of the invention]” and insert --DETAILED DESCRIPTION OF THE EMBODIMENTS--.

<u>IN THE CLAIMS:</u>

Please amend the claims as follows.

Claim 1, line 5 (of the claim), change “chosen” to --selected--.

Claim 2, line 1, delete “in which” and insert --wherein--; and
line 2, change “chosen” to --selected--.

Claim 3, line 1, delete “or 2”.

Claim 4, line 1, delete “any one of the preceding claims, in which" and insert --Claim 1--.

Claim 5, lines 1 and 2, delete “any one of the preceding claims, in which" and insert --Claim 1, wherein--.

Claim 6, lines 1 and 2, delete “any one of the preceding claims, in which" and insert --Claim 1, wherein--; and
line 4, delete “, preferably 5 to 40%,”.

Claim 7, line 1, delete “any one of Claims 1 to 5, in which” and insert --Claim 1, wherein--.

Claim 8, line 1, delete “any one of the preceding claims” and insert --Claim 1--.

Claim 9, lines 1 and 2, delete " "any one of the preceding claims, in which" and insert --Claim 1, wherein--; and

line 2, delete "such".

Claim 10, line 3, change "chosen" to --selected--.

Please add new claim 11, as follows.

--11.(New) Compositions according to Claim 6, wherein the amount of alky (meth)acrylate is 5 to 40% by weight.--

REMARKS

The above amendments to the specification and claims are made to conform the application to U.S. format, and to remove multiple dependency and improper language from the claims. New claim 11 is added to re-introduce the disclosure cancelled from claim 6 herein. No new matter is added by these amendments.

Approval and entry of the requested amendments are courteously solicited.

Respectfully submitted,
SMITH, GAMBRELL & RUSSELL, LLP
Beveridge, DeGrandi, Weilacher & Young
Intellectual Property Group

By: _____
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Date: 24 November 2000

ABSTRACT

THERMOPLASTIC POLYESTER COMPOSITIONS HAVING IMPROVED IMPACT PROPERTIES

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4 & 8 Cours Michelet
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92800 PUTEAUX - Hauts-de-Seine

Agent: Henry NÉEL

Inventors: Mr Christophe LACROIX
Mr Alain BOUILLOUX

The present invention relates to thermoplastic polyesters, which comprise, by weight:

(i) a thermoplastic polyester;

(ii) an impact modifier comprising:

(a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

(iii) the (B)/(A) ratio being between 40/60 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively;

(iv) the (B)/(A) ratio being between 40/60 and 25/75 for proportions of impact modifier between 2 and 18% in 98 to 82% of polyester, respectively. It is particularly useful for PET and PBT.

THERMOPLASTIC POLYESTER COMPOSITIONS HAVING IMPROVED IMPACT PROPERTIES

[Field of the invention]

The present invention relates to thermoplastic polyesters having improved impact properties and to impact-modifier compositions.

Thermoplastic polyesters, such as PBT (polybutylene terephthalate) and PET (polyethylene terephthalate) possess excellent dimensional-stability, heat-resistance and chemical-resistance properties and are used in the electrical, electronic and motor-vehicle fields. However, at high temperature, during conversion operations, a reduction in the molecular weight of the polymer may occur, leading to a reduction in the impact properties. In addition, polyesters have poor fracture-resistance properties in the case of notched components.

The present invention provides thermoplastic polymers in which an impact-modifier composition is added in order to obtain improved impact properties, especially low-temperature toughness. The present invention also relates to this impact-modifier composition that is added to the polyesters to improve the impact properties thereof. These modifier compositions make it possible to achieve impact properties superior to those obtained with each of the compounds separately.

[Prior art]

Patent US 4,753,890 (= EP 174,343) describes polyesters, such as, for example, polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), which are modified by ethylene-alkyl (meth)acrylate-glycidyl (meth)acrylate copolymers.

Patent US 5,369,154 describes PET/polycarbonate blends containing four different modifiers: a copolymer comprising an epoxide, a copolymer of the core-shell type, an SBR- or SBS- or EPR-type elastomer and a copolymer

of the SAN or ABS type. These core-shell copolymers comprise fine particles having an elastomer core and a thermoplastic shell.

Patent EP 115,015 describes PET or PBT containing linear low-density polyethylene (LLDPE), glass fibres and optionally a core–shell copolymer.

Patent EP 133,993 describes PET containing a core–shell copolymer and a copolymer of ethylene with either an alkyl acrylate or (meth)acrylic acid.

Japanese Patent Application JP 01,247,454 A, published on 3 October 1989 describes PBT containing an ethylene-alkyl (meth)acrylate copolymer and an ethylene-glycidyl methacrylate copolymer.

Patents EP 838,501 and EP 511,475 describe compositions similar to those of the above Japanese application.

Patent EP 803,537 describes PET and polycarbonate containing a copolymer comprising glycidyl methacrylate. Firstly, the polycarbonate and the copolymer comprising glycidyl methacrylate are blended together and then this blend is incorporated into the PET.

Patent EP 187,650 describes PET containing a core–shell copolymer and a copolymer of ethylene with either maleic anhydride or a (meth)acrylic acid.

Patent EP 737,715 describes PBTs modified by an impact modifier consisting of an ethylene-methyl methacrylate-glycidyl methacrylate copolymer/core–shell copolymer blend. The amount of impact modifier is from 5 to 20 parts per 100 parts of polyester, i.e. 4.8 to 16.7% for 95.2 to 83.7% of polyester, respectively. The proportions of the glycidyl methacrylate copolymer to the core–shell copolymer are in the ratio 15/85 to 20/80. In the examples, the amount of impact modifier is from 18 parts per 100 parts of polyester, i.e. 15.3%, and the proportion of glycidyl methacrylate copolymer to the core–shell copolymer is in the ratio 3/15, i.e. 17/83.

Patent EP 531,008 describes spent (recycled) PBT/polycarbonate (PC) blends containing core–shell copolymers, to which functionalized copolymers are added in order to make them into a new thermoplastic.

These functionalized copolymers are either ethylene-glycidyl methacrylate (GMA) copolymers or ethylene–vinyl acetate-glycidyl methacrylate copolymers. The description quotes proportions of 1 to 97% of polycarbonate, from 1 to 97% of PBT, 1 to 40% of core–shell copolymer and 1 to 40% of glycidyl methacrylate copolymer. In fact, the PBT/polycarbonate blends that it is desired to recycle contain, according to the examples, 15% of core–shell copolymer, which corresponds to more realistic values. Blends (i) of 80 parts of recycled material with 20 parts of glycidyl methacrylate copolymer and blends (ii) of 90 parts of recycled material with 10 parts of glycidyl methacrylate copolymer are then made. The proportions are in the EP 531,008 table below, in which the parts are by weight:

TABLE EP 531 008

	Compositions such that the core-shell copolymer/PC+PBT ratio = 15/85		
PC+PBT	85	68	76.5
Core–shell copolymer (CS)	15	12	13.5
GMA copolymer		20	10
PC+PBT+CS+ GMA copolymer	100	100	100
GMA/CS copolymer		20/12 =(62/38)	10/13.5 =(43/57)
Proportion of modifier (Core–shell copolymer + GMA copolymer) in PC+PBT		20+12=32%	10+13.5=23.5%

[The technical problem]

It has been seen from the prior art that saturated polyesters can have their impact properties improved by the addition of a core-shell copolymer. These polymers have a particularly well defined structure in which the core consists of a polymer having an elastomeric character and

the shell has a thermoplastic character. It has also been seen that the improvement in impact strength may be obtained by also incorporating a dispersed phase of an impact modifier optionally containing reactive functional groups capable of reacting with the functional groups of the polyesters. This reactivity makes it possible to ensure a fine and homogeneous dispersion of the modifier as well as good adhesion. The core-shell copolymer may itself also be functionalized in order to allow better adhesion to the matrix. However, this reactivity is sometimes high and may lead to a reduction in the melt flow index. This reduction in the melt flow index is prejudicial to the injection moulding of large parts or of fine parts.

It has now been found that it is possible to improve the impact properties of thermoplastic polyesters by adding two kinds of modifier to them, namely (a) a core–shell copolymer and (b) either an ethylene-unsaturated epoxide copolymer or an ethylene–carboxylic acid anhydride copolymer, or a blend of these but in proportions in the polyester and in (b)/(a) ratios which are different from those of the prior art EP 737,715 and EP 531,008. Better impact strength is obtained, while maintaining and even improving the melt flow index.

[Brief description of the invention]

The present invention relates to thermoplastic polyester compositions com prising, by weight:

(i) a thermoplastic polyester;

(ii) an impact modifier comprising:

(a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

(iii) the (B)/(A) ratio being between 40/60 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively;

(iv) the (B)/(A) ratio being between 40/60 and 25/75 for proportions of impact modifier between 2 and 18% in 98 to 82% of polyester, respectively, and advantageously between 5 and 18% in 95 to 82% of polyester, respectively.

The present invention also relates to an impact-modifier composition which can be added to the thermoplastic polyesters to improve their impact properties and comprising:

(a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1) and ethylene-unsaturated epoxide copolymers (B2);

- the (B)/(A) ratio being between 40/60 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively,
- the (B)/(A) ratio being between 40/60 and 25/75 for proportions of impact modifier between 2 and 18% in 98 to 82% of polyester, respectively, and advantageously between 5 and 18% in 95 to 82% of polyester, respectively.

[Detailed description of the invention]

The term "thermoplastic polyester" denotes polymers which are saturated products coming from the condensation of glycols and of dicarboxylic acids, or of their derivatives. Preferably, they comprise the products of the condensation of aromatic dicarboxylic acids having from 8 to 14 carbon atoms and of at least one glycol chosen from the group consisting of neopentyl glycol, cyclohexanedimethanol and aliphatic glycols of formula $HO(CH_2)_nOH$ in which n is an integer ranging from 2 to 10. Up to 50 mol% of the aromatic dicarboxylic acid may be replaced with at least one other aromatic dicarboxylic acid having from 8 to 14 carbon atoms, and/or up to 20 mol% may be replaced with an aliphatic dicarboxylic acid having from 2 to 12 carbon atoms.

The preferred polyesters are polyethylene terephthalate (PET), poly(1,4-butylene) terephthalate (PBT), 1,4-cyclohexylene dimethylene terephthalate/isophthalate) and other esters derived from aromatic dicarboxylic acids such as isophthalic acid, dibenzoic acid, naphthalene dicarboxylic acid, 4,4'-diphenylenedicarboxylic acid, bis(p-carboxyphenyl)methane acid, ethylene bis(p-benzoic) acid, 1,4-tetramethylene bis(p-oxybenzoic) acid, ethylene bis(para-oxybenzoic) acid, 1,3-trimethylene bis(p-oxybenzoic) acid, and glycols such as ethylene glycol, 1,3-trimethylene glycol, 1,4-tetramethylene glycol, 1,6-hexamethylene glycol, 1,3-propylene glycol, 1,8-octamethylene glycol and 1,10-decamethylene glycol. The MFI of these polyesters, measured at 250°C and with 2.16 kg, may vary from 2 to 100 and advantageously from 10 to 80. "MFI" denotes the melt flow index.

It would not be outside the scope of the invention if the polyesters consisted of several diacids and/or several diols. It is also possible to use a blend of various polyesters.

It would not be outside the scope of the invention if the polyesters contained copolyetheresters. These copolyetheresters are copolymers containing polyester blocks and polyether blocks having polyether units derived from polyetherdiols such as polyethylene glycol (PEG), polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), dicarboxylic acid units such as terephthalic acid units, and short, chain-extender, diol units such as glycol (ethanediol) or 1,4-butanediol. The linking of the polyethers with the diacids forms the flexible segments whereas the linking of the glycol or butanediol with the diacids forms the rigid segments of the copolyetherester. These copolyetheresters are thermoplastic elastomers. The proportion of these copolyetheresters may represent up to 30 parts per 100 parts of thermoplastic polyester.

It would not be outside the scope of the invention if the polyesters contained polycarbonate. In general, the term "polycarbonate" denotes polymers comprising the following units:

$$-O-R_1-O-\overset{\displaystyle O}{\overset{\|}{C}}-$$

in which R_1 is an aliphatic, alicyclic or aromatic divalent group; the aliphatic and alicyclic groups may contain up to 8 carbon atoms. By way of example of R_1, mention may be made of ethylene, propylene, trimethylene, tetramethylene, hexamethylene, dodecamethylene, poly(1,4-[2-butenylene]), poly(1,10-[(2-ethyldecylene]), 1,3-cyclopentylene, 1,3-cyclohexylene, 1,4-cyclohexylene, m-phenylene, p-phenylene, 4,4'-diphenylene, 2,2-bis(4-phenylene)propane and benzene-1,4-dimethylene. Advantageously, at least 60% of the R_1 groups in the polycarbonate and preferably all the groups R_1 are aromatic groups of formula:

$$-R_2-Y-R_3-$$

in which R_2 et R_3 are divalent monocyclic aromatic radicals and Y is a linking radical in which one or two atoms separate R_2 and R_3. The free valences are generally in the meta or para position with respect to Y. R_2 and R_3 may be substituted or unsubstituted phenylenes; as substituents, mention may be made of alkyl, alkenyl, halogen, nitro and alkoxy. Preferably, the phenylenes are unsubstituted; they may be together or separately meta or para and are preferably para. The linking radical Y is preferably such that one atom separates R_2 from R_3 and is preferably a hydrocarbon radical such as methylene, cyclohexylmethylene, 2-[2.2.1]bicycloheptylmethylene, ethylene, 2,2-propylene, 1,1-(2,2-dimethylpropylene), 1,1-cyclohexylene, 1,1-cyclopentadecylene, cyclododecylene, carbonyl, the oxy radical, the thio radical and sulfone. Preferably, R_1 is 2,2-bis(4-phenylene)propane which comes from bisphenol A, that is to say Y is isopropylidene and R_2 and R_3 are each p-phenylene.

Advantageously, the intrinsic viscosity of the polycarbonate, measured in methylene chloride at 25°C, is between 0.3 and 1 dl/g.

The proportion of polycarbonate may represent up to 30 parts per 100 parts of thermoplastic polyester.

With regard to the core-shell copolymer (A), this is in the form of fine particles having an elastomer core and at least one thermoplastic shell, the particle size being generally less than 1 µm and advantageously between 200 and 500 nm. By way of example of the core, mention may be made of isoprene homopolymers or butadiene homopolymers, copolymers of isoprene with at most 30 mol% of a vinyl monomer and copolymers of butadiene with at most 30 mol% of a vinyl monomer. The vinyl monomer may be styrene, an alkylstyrene, acrylonitrile or an alkyl (meth)acrylate. Another core family consists of the homopolymers of an alkyl (meth)acrylate and the copolymers of an alkyl (meth)acrylate with at most 30 mol% of a vinyl monomer. The alkyl (meth)acrylate is advantageously butyl acrylate. The vinyl monomer may be styrene, an alkylstyrene, acrylonitrile, butadiene or isoprene. The core of the copolymer (A) may be completely or partly crosslinked. All that is required is to add at least difunctional monomers during the preparation of the core; these monomers may be chosen from poly(meth)acrylic esters of polyols, such as butylene di(meth)acrylate and trimethylolpropane trimethacrylate. Other difunctional monomers are, for example, divinylbenzene, trivinylbenzene, vinyl acrylate and vinyl methacrylate. The core can also be crosslinked by introducing into it, by grafting or as a comonomer during the polymerization, unsaturated functional monomers such as anhydrides of unsaturated carboxylic acids, unsaturated carboxylic acids and unsaturated epoxides. Mention may be made, by way of example, of maleic anhydride, (meth)acrylic acid and glycidyl methacrylate.

The shell(s) are styrene homopolymers, alkylstyrene homopolymers or methyl methacrylate homopolymers, or copolymers comprising at least 70 mol% of one of the above monomers and at least one comonomer chosen from the other above monomers, vinyl acetate and acrylonitrile. The shell may be functionalized by introducing into it, by grafting or as a

comonomer during the polymerization, unsaturated functional monomers such as anhydrides of unsaturated carboxylic acids, unsaturated carboxylic acids and unsaturated epoxides. Mention may be made, for example, of maleic anhydride, (meth)acrylic acid and glycidyl methacrylate. By way of example, mention may be made of core-shell copolymers (A) having a polystyrene shell and core-shell copolymers (A) having a PMMA shell. There are also core-shell copolymers (A) having two shells, one made of polystyrene and the other, on the outside, made of PMMA. Examples of copolymers (A) and their method of preparation are described in the following patents: US 4,180,494, US 3,808,180, US 4,096,202, US 4,260,693, US 3,287,443, US 3,657,391, US 4,299,928 and US 3,985,704.

Advantageously, the core represents, by weight, 70 to 90% of (A) and the shell represents 30 to 10%.

By way of example of a copolymer (A), mention may be made of that consisting (i) of 75 to 80 parts of a core comprising at least 93 mol% of butadiene, 5 mol% of styrene and 0.5 to 1 mol% of divinylbenzene and (ii) of 25 to 20 parts of two shells essentially of the same weight, the inner one made of polystyrene and the outer one made of PMMA.

With regard to ethylene-unsaturated carboxylic acid anhydride copolymers (B1), these may be polyethylenes grafted by an unsaturated carboxylic acid anhydride or ethylene-unsaturated carboxylic acid anhydride copolymers which are obtained, for example, by radical polymerization.

The unsaturated carboxylic acid anhydride may be chosen, for example, from maleic, itaconic, citraconic, allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4—methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic and x—methylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic anhydrides. Advantageously, maleic anhydride is used. It would not be outside the scope of the invention to replace all or part of the anhydride with an unsaturated carboxylic acid such as, for example, (meth)acrylic acid.

With regard to the polyethylenes onto which the unsaturated carboxylic acid anhydride is grafted, the term "polyethylene" should be understood to mean homopolymers or copolymers.

By way of comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms; by way of examples of alpha-olefins, mention may be made of propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1—eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1—octacocene and 1-triacontene; these alpha-olefins may be used separately or as a mixture of two or more of them;
- esters of unsaturated carboxylic acids, such as, for example, alkyl (meth)acrylates, the alkyls possibly having up to 24 carbon atoms; examples of alkyl acrylates or methacrylates are especially methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;
- vinyl esters of saturated carboxylic acids, such as, for example, vinyl acetate or vinyl propionate;
- dienes such as, for example, 1,4-hexadiene.

The polyethylene may include several of the above comonomers.

Advantageously, the polyethylene, which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of ethylene and its density may be between 0.86 and 0.98 g/cm^3. The MFI (Melt Flow Index at 190°C/2.16 kg) is advantageously between 0.1 and 1000 g/10 min.

By way of example of polyethylenes, mention may be made of:

- low-density polyethylene (LDPE)
- high-density polyethylene (HDPE)
- linear low-density polyethylene (LLDPE)
- very low-density polyethylene (VLDPE)
- polyethylene obtained by metallocene catalysis, that is to say polymers obtained by the copolymerization of ethylene and of an alpha-olefin such as propylene, butene, hexene or octene in the presence of a single-site catalyst generally consisting of a zirconium or titanium atom and of two

alkyl cyclic molecules linked to the metal. More specifically, the metallocene catalysts are usually composed of two cyclopentadiene rings linked to the metal. These catalysts are frequently used with aluminoxanes as cocatalysts or activators, preferably methylaluminoxane (MAO). Hafnium may also be used as the metal to which the cyclopentadiene is fixed. Other metallocenes may include transition metals of Groups IV A, V A and VI A. Metals from the series of lanthamides may also be used.

- EPR (ethylene-propylene-rubber) elastomers;
- EPDM (ethylene-propylene-diene) elastomers;
- blends of polyethylene with an EPR or an EPDM;
- ethylene-alkyl (meth)acrylate copolymers possibly containing up to 60%, and preferably 2 to 40%, by weight of (meth)acrylate.

The grafting is an operation known per se.

With regard to the ethylene-unsaturated carboxylic acid anhydride copolymers, that is to say those in which the unsaturated carboxylic acid anhydride is not grafted, these are copolymers of ethylene, the unsaturated carboxylic acid anhydride and, optionally another monomer which may be chosen from the comonomers that were mentioned above in the case of the ethylene copolymers intended to be grafted.

Advantageously, ethylene-maleic anhydride copolymers and ethylene-alkyl (meth)acrylate-maleic anhydride copolymers are used. These copolymers comprise from 0.2 to 10% by weight of maleic anhydride and from 0 to 40%, preferably 5 to 40%, by weight of alkyl (meth)acrylate. Their MFIs are between 0.5 and 200 (190°C/2.16 kg). The alkyl (meth)acrylates have already been described above. It is possible to use a blend of several copolymers (B1), and it is also possible to use an ethylene-maleic anhydride copolymer/ethylene-alkyl (meth)acrylate-maleic anhydride copolymer blend.

The copolymer (B1) is commercially available, produced by radical polymerization at a pressure which may range between 200 and 2500 bar and is sold in the form of granules.

With regard to the ethylene-unsaturated epoxide copolymers (B2), these may be obtained by the copolymerization of ethylene with an

unsaturated epoxide or by grafting the unsaturated epoxide to the polyethylene. The grafting may be carried out in the solvent phase or onto the polyethylene in the melt in the presence of a peroxide. These grafting techniques are known per se. With regard to the copolymerization of ethylene with an unsaturated epoxide, it is possible to use so-called radical polymerization processes usually operating at pressures between 200 et 2500 bar.

By way of example of unsaturated epoxides, mention may be made of:

- aliphatic glycidyl esters and ethers, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate, glycidyl itaconate, glycidyl acrylate and glycidyl methacrylate; and
- alicyclic glycidyl esters and ethers, such as 2-cyclohex-1-ene glycidyl ether, diglycidyl cyclohexene-4-5-dicarboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl *endo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate.

With regard to grafting, the copolymer is obtained by grafting an ethylene homopolymer or copolymer as described in the case of (B1), except that an epoxide is grafted instead of an anhydride. With regard to copolymerization, this is also similar to (B1) except that an epoxide is used; it may also have other comonomers, as in the case of (B1).

The product (B2) is advantageously an ethylene-alkyl (meth)acrylate–unsaturated epoxide copolymer or an ethylene–unsaturated epoxide copolymer. Advantageously, it may contain up to 40%, preferably 5 to 40%, by weight of alkyl (meth)acrylate and up to 10%, preferably 0.1 to 8%, by weight of unsaturated epoxide.

Advantageously, the epoxide is glycidyl (meth)acrylate.

Advantageously, the alkyl (meth)acrylate is chosen from methyl (meth)acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate. The amount of alkyl (meth)acrylate is advantageously from 20 to 35%. The MFI is advantageously between 0.5 and 200 (in g/10 min. at 190°C/2.16 kg). It is possible to use a blend of several copolymers (B2), and it is also possible to use an ethylene-alkyl

(meth)acrylate–unsaturated epoxide copolymer/ethylene-unsaturated epoxide copolymer blend. It is also possible to use blends of (B1) and (B2).

This copolymer (B2) may be obtained by radical polymerization of the monomers.

Advantageously, the thermoplastic polyester compositions of the invention comprise, per 100 parts by weight, 75 to 95 parts of polyester for 25 to 5 parts of impact modifier, respectively.

Advantageously, the proportions of (A) and (B) are such that the (B)/(A) ratio is between 40/60 and 25/75, whatever the amount of impact modifier in the polyester.

Among the copolymers (B), it is advantageous to use the copolymers (B2).

The invention also relates to an impact-modifier composition having these proportions.

The thermoplastic polyesters of the invention may also include, in addition to the impact modifier, slip agents, antiblocking agents, antioxidants, UV stabilizers and fillers. The fillers may be glass fibres, fire retardants, talc or chalk.

The thermoplastic polyester/impact-modifier blends are prepared by the usual techniques for thermoplastic polymers in single-screw or twin-screw extruders, mixers or apparatuses of the BUSS® Ko-kneader type. The polyester and the constituents of the impact modifier, namely the copolymers (A), (B) and (C), may be introduced separately into the blending device. The constituents of the impact modifier may also be added in the form of a blend prepared in advance, possibly in the form of a masterbatch in the polyester. The additives may be added into these apparatuses, such as the slip agents, the antiblocking agents, the antioxidants, the UV stabilizers and the fillers, whether as they are or in the form of a masterbatch in the polyester or else in the form of a masterbatch with one or more of the copolymers (A) to (C). The impact-modifier composition comprising (A) to (C) which may be added to the polyesters is also prepared by the previous usual technique of blending thermoplastic polymers.

[Examples]

The following products were used:

AX 8900: ethylene-methyl acrylate-glycidyl methacrylate (GMA) copolymer comprising, by weight, 25% acrylate and 8% GMA, having an MFI of 6 (190°C/2.16 kg). It is sold under the brand name LOTADER® par Elf Atochem;

AX 8930: ethylene-methyl acrylate-glycidyl methacrylate (GMA) copolymer comprising, by weight, 25% acrylate and 3% GMA, having an MFI of 6 (190°C/2.16 kg). It is sold under the brand name LOTADER® par Elf Atochem;

E920: MBS-type core–shell copolymer with a core essentially based on butadiene-styrene and a shell of PMMA, sold by Elf Atochem under the brand name METABLEND®;

EXL 2314: epoxy-functionalized acrylic core–shell copolymer sold by Röhm and Haas under the brand name PARALOID®;

PBT: polybutylene terephthalate having an MFI of 20 (250°C/2.16 kg) sold by BASF under the brand name ULTRADUR® B4500.

All the examples were produced with compositions comprising 80% by weight of PBT and 20% by weight of impact modifier. The notched Charpy impact strength complies with the ISO 179:93 standard; the higher the value the better the impact strength.

FIGURE 1 shows the notched Charpy impact strength at -40°C for PBT containing impact modifier consisting either of AX or of core-shell copolymer or of their blends. Two kinds of AX: AX 8900 and AX 8930 and two kinds of core-shell copolymer: EXL 2314 and E920 were used. **FIGURE 2** shows the impact strengths of these same compositions at +23°C. In these figures and in the tables, the epoxide copolymer has been denoted by AX and the core-shell copolymer by CS. The AX/CS ratio is the

weight ratio, "30/70" meaning 30 parts of AX to 70 parts of CS. The values are also given in **TABLE 1** and **TABLE 2**.

TABLE 1

PBT+20%(AX+CS) AX=AX 8900 or AX 8930 CS=EXL 2314 or E920	Notched Charpy impact strength at –40°C			
	AX 8900 EXL 2314	AX 8900/E920	AX 8930 EXL 2314	AX 8930/E920
100/0 AX/CS (comparative)	6.2	6.2	5	5
70/30 AX/CS (comparative)	9.8	10	8.8	9.9
30/70 AX/CS	7.8	14.75	7.1	9.8
20/80 AX/CS	9.2	10.25		
10/90 AX/CS		13.8		
0/100 AX/CS (comparative)	6.75	8.2	6.75	8.2

TABLE 2

PBT+20%(AX+CS) AX=AX 8900 or AX 8930 CS=EXL 2314 or E920	Notched Charpy impact strength at +23°C			
	AX 8900 EXL 2314	AX 8900/E920	AX 8930 EXL 2314	AX 8930/E920
100/0 AX/CS (comparative)	76.4	76.4	55.2	55.2
70/30 AX/CS (comparative)	99	62.2	67.5	61
30/70 AX/CS	91.8	88.9	82.6	88.4
20/80 AX/CS	87.6	79.5		
10/90 AX/CS		80		
0/100 AX/CS (comparative)	62	18	62	18

FIGURE 3 shows the MFI of the above compositions containing the various impact modifiers and also the MFI of the PBT without a modifier: "pure PBT". The values are also given in **TABLE 3** below.

TABLE 3

PBT+20%(AX+CS) AX=AX 8900 or AX 8930 CS=EXL 2314 or E920	MFI (250°C/2.16 kg) no change with the type of AX and CS

100/0 AX/CS (comparative)	0.63
70/30 AX/CS (comparative)	0.9
30/70 AX/CS	1.63
20/80 AX/CS	3.5
10/90 AX/CS	3
0/100 AX/CS (comparative)	7.4
Pure PBT (comparative)	20

It is within the skill in the art to practice this invention in numerous modifications and variations in light of the above teachings. Therefore, it is understood that the various embodiments of this invention described herein may be altered without departing from the spirit and scope of this invention as defined by the appended claims.

CLAIMS

1 Thermoplastic polyester compositions comprising, by weight:

(i) a thermoplastic polyester;

(ii) an impact modifier comprising:

(a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

(iii) the (B)/(A) ratio being between 40/60 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively;

(iv) the (B)/(A) ratio being between 40/60 and 25/75 for proportions of impact modifier between 2 and 18% in 98 to 82% of polyester, respectively, and advantageously between 5 and 18% in 95 to 82% of polyester respectively.

2 Compositions according to Claim 1, in which the polyester is chosen from PET and PBT.

3 Compositions according to Claim 1 or 2, comprising up to 30 parts by weight of copolyetherester per 100 parts of thermoplastic polyester.

4 Compositions according to any one of the preceding claims, comprising up to 30 parts by weight of polycarbonate per 100 parts of thermoplastic polyester.

5 Compositions according to any one of the preceding claims, in which the copolymer (A) comprises an elastomer core and at least one thermoplastic shell.

6 Compositions according to any one of the preceding claims, in which the copolymers (B1) are ethylene-alkyl (meth)acrylate-maleic anhydride copolymers which comprise from 0.2 to 10% by weight of maleic anhydride and from 0 to 40%, preferably 5 to 40%, by weight of alkyl (meth)acrylate.

7 Compositions according to any one of Claims 1 to 5, in which the ethylene-unsaturated epoxide copolymers (B2) are ethylene-alkyl (meth)acrylate-unsaturated epoxide copolymers obtained by copolymerization of the monomers and contain from 0 to 40% by weight of alkyl (meth)acrylate and up to 10% by weight of unsaturated epoxide.

8 Compositions according to any one of the preceding claims, comprising, per 100 parts by weight, 75 to 95 parts of polyester for 25 to 5 parts of impact modifier, respectively.

9 Compositions according to any one of the preceding claims, in which the proportions of (A) and (B) are such that the (B)/(A) ratio is between 40/60 and 25/75, whatever the amount of impact modifier in the polyester.

10 Impact-modifier compositions comprising:

(a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

- the (B)/(A) ratio being between 40/60 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively,
- the (B)/(A) ratio being between 40/60 and 25/75 for proportions of impact modifier between 2 and 18% in 98 to 82% of polyester, respectively, and advantageously between 5 and 18% in 95 to 82% of polyester, respectively.

FIGURE 1

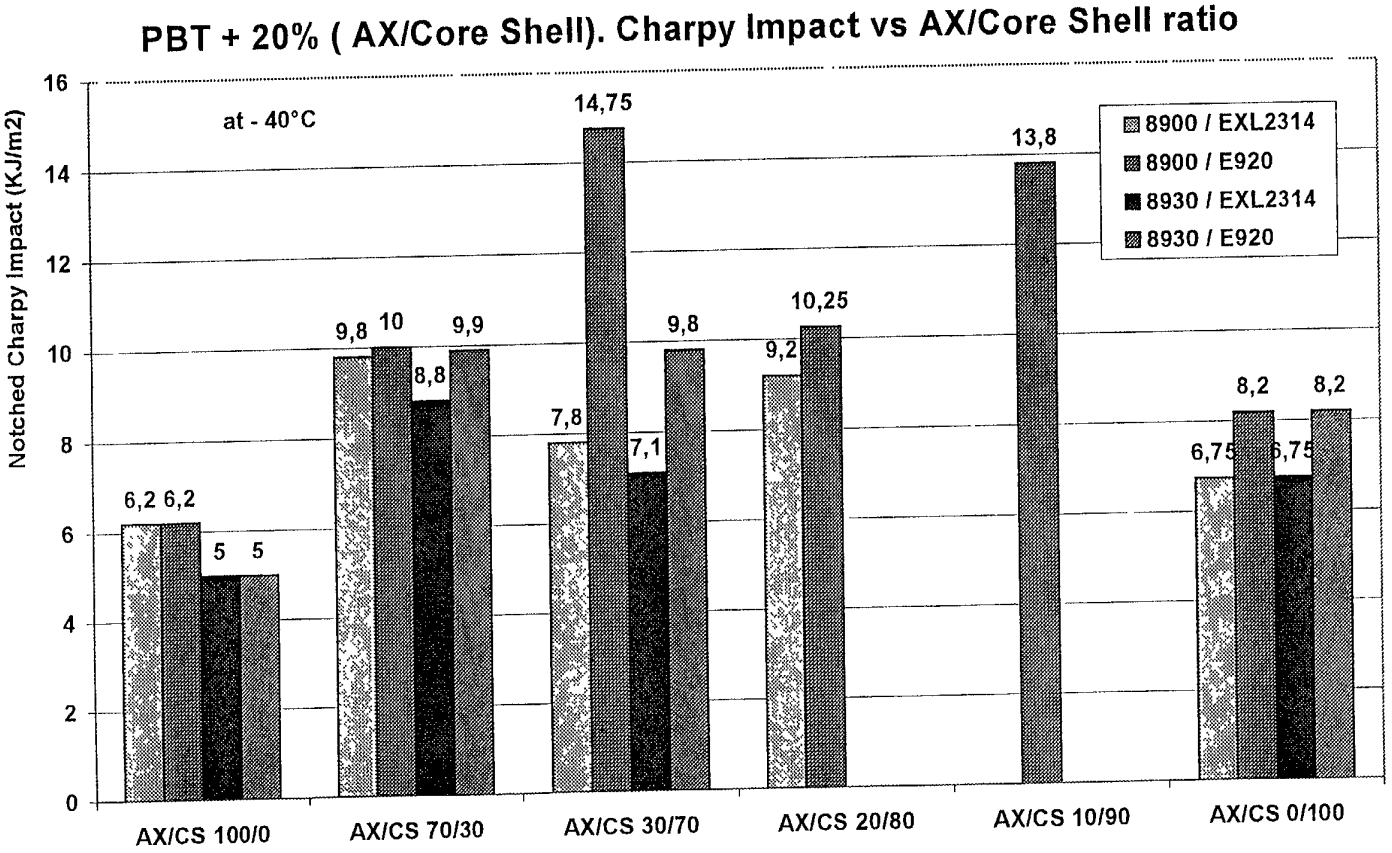

FIGURE 2

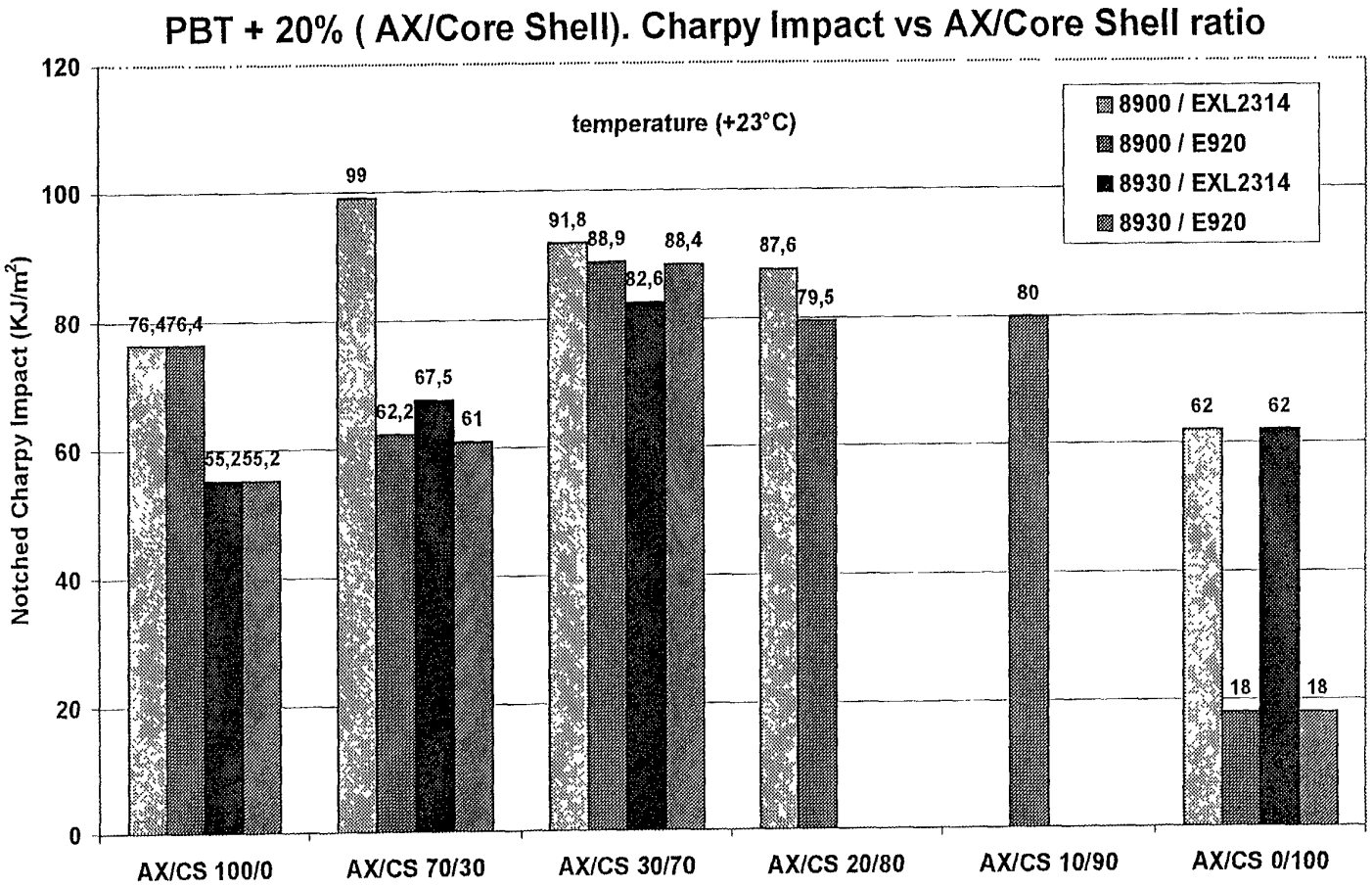
PBT + 20% (AX/Core Shell). Charpy Impact vs AX/Core Shell ratio
temperature (+23°C)
8900 / EXL2314
8900 / E920
8930 / EXL2314
8930 / E920
Notched Charpy Impact (KJ/m²)
120
100
80
60
40
20
0
76,4
76,4
55,2
55,2
99
62,2
67,5
61
91,8
88,9
82,6
88,4
87,6
79,5
80
62
18
62
18
AX/CS 100/0
AX/CS 70/30
AX/CS 30/70
AX/CS 20/80
AX/CS 10/90
AX/CS 0/100

FIGURE 3